

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
31.01.1996 Bulletin 1996/05

(51) Int Cl.⁶ C10G 69/04, C10G 11/05

(21) Application number: 89203038.8

(22) Date of filing: 29.11.1989

(54) **Process for the conversion of a hydrocarbonaceous feedstock**
Kohlenwasserstoffumwandlungsverfahren
Procédé de conversion d'hydrocarbures

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(30) Priority: 02.12.1988 GB 8828206

(43) Date of publication of application:
13.06.1990 Bulletin 1990/24

(73) Proprietor:
SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
NL-2596 HR Den Haag (NL)

(72) Inventors:

- Maxwell, Ian Ernest
NL-1031 CM Amsterdam (NL)
- Biswas, Jaydeep
NL-1031 CM Amsterdam (NL)
- Minderhoud, Johannes Kornelis
NL-1031 CM Amsterdam (NL)

(56) References cited:

EP-A- 0 125 709	EP-A- 0 347 003
US-A- 3 420 770	US-A- 3 856 659
US-A- 4 171 257	US-A- 4 502 945

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 372 632 B1

The present invention relates to a process for the conversion of a hydrocarbonaceous feedstock and is particularly concerned with the upgrading of certain feedstocks.

US 4,171,257 describes a process for upgrading a hydrocarbonaceous feedstock by contacting the feedstock with a ZSM-5 crystalline aluminosilicate catalyst at a pressure below 14 bar, a temperature of 260 to 427 °C and a space velocity of 0.1 to 15 l/h. The feedstock, exemplified as gas oil having a boiling point range of 230 to 437 °C, must contain less than 5 ppmw of nitrogen-containing compounds, calculated as nitrogen. The upgraded product includes olefinic hydrocarbons, such as propene and butenes.

US 4,502,945 describes a dewaxing process for upgrading a paraaffinic hydrocarbonaceous feedstock by contacting the feedstock with an intermediate pore size zeolite at a pressure of 1 to 8 bar, a temperature of 290 to 595°C, preferably of 340 to 480°C, and a space velocity of 0.1 to 50 v/v/hr. The zeolite must have a silica:alumina mole ratio from about 175:1 to about 300:1 and is preferably ZSM-5. The upgraded product includes olefinic hydrocarbons such as propene and butenes.

US 3,856,659 describes a multistage hydrocarbon conversion operation in the presence of a dual cracking catalyst composition comprising ZSM-5 material, for the production of gasoline and olefinic components, employing one or more riser reactors in parallel flow arrangement wherein the larger and smaller pore catalytic cracking materials comprising the dual function catalyst work substantially independently in their restructuring of hydrocarbon constituents coming in contact therewith under particularly selected operating conditions. Particularly a first hydrocarbon feed contacts the dual function catalyst in a riser conversion zone, the dual function Catalyst is then contacted with a second hydrocarbon feed more refractory than the first under conditions to substantially deactivate the cracking activity of the large pore catalyst component without undesirably influencing the activity of the small pore catalyst component which can then be contacted with low boiling hydrocarbon components to effect their restructuring to cyclic components of relatively high octane rating.

The production of olefins is desirable as their reactivity renders them suitable for conversion to further products, in contrast to the low value lower paraffins. However, the above described process has the drawback that the initial feedstock must have been severely denitrified in order to avoid rapid catalyst deactivation.

It has surprisingly been found that a comparatively high yield of olefins can be obtained, under less stringent conditions as regards nitrogen content, using certain zeolitic catalysts, at high temperature with a short feedstock residence time. Furthermore, it has been surprisingly found that the conversion is suitable for heavy hydrocarbon feedstocks and an upgraded product rich in lower olefins can be obtained therefrom.

Accordingly, the present invention provides a process for the conversion of a hydrotreated and/or hydrocracked heavy hydrocarbonaceous feedstock to obtain a high proportion of olefinically unsaturated gaseous products, which process comprises contacting the feedstock in a single stage with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.4 to 0.7 nm wherein the contacting is carried out at a catalyst/feedstock weight ratio from 2 to 200, a temperature of greater than or equal to 480 °C and a pressure of up to 10 bar during less than 10 seconds.

The feedstock is contacted with the zeolitic catalyst for less than 10 seconds. Suitably, the minimum contact time is 0.1 second. Very good results are obtainable with a process in which the feedstock is contacted with the zeolitic catalyst during 1 to 6 seconds.

The temperature during the reaction is relatively high. However, the combination of high temperature and short residence time allows a high conversion to olefins. A preferred temperature range is 480 to 900 °C, more preferably 500 to 750 °C.

The zeolitic catalyst comprises a zeolite with a pore diameter of from 0.4 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably 50:50 to 85:15. The catalyst may comprise further zeolites with a pore diameter above 0.7 nm. Suitable examples of such zeolites include the faujasite-type zeolites, zeolite beta, zeolite omega and in particular zeolite X and Y. The zeolitic catalyst preferably comprises as zeolite substantially only zeolites with a pore diameter of from 0.4 to 0.7 nm.

The term zeolite in this specification is not to be regarded as comprising only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates.

Examples of zeolites that may be used in the process of the invention and that have a pore diameter of 0.4 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates

with ZSM-5 structure are aluminium, gallium, iron, scandium, niobium and/or scandium silicates as described in e.g. GB-B-2,110,559.

During the preparation of the zeolites usually a significant amount of alkali metal oxide is present in the prepared zeolite. Preferably the amount of alkali metal is removed by methods known in the art, such as ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. Preferably the zeolite used in the present process is substantially in its hydrogen form.

Olefin production is facilitated by the absence of hydrogen or a hydrogen donor. Hence, the present process is advantageously carried out in the absence of added hydrogen and/or steam. It is, of course, possible that during the reaction some small molecules, such as hydrogen molecules are formed. However, this amount is usually negligible and will be less than 0.5 %wt of the product.

The pressure in the present process can be varied within wide ranges. It is, however, preferred that the pressure is such that at the prevailing temperature the feedstock is substantially in its gaseous phase. Then it is easier to achieve the short contact times envisaged. Hence, the pressure is preferably relatively low. This is the more advantageous since no expensive compressors and high-pressure vessels and other equipment are necessary. Pressures up to 10 bar can be employed. Subatmospheric pressures are possible, but not preferred. The minimum pressure is suitably 1 bar. It is economically advantageous to operate at atmospheric pressure.

The catalyst/feedstock weight ratio may vary widely, for example up to 200 kg of catalyst per kg of feedstock. Preferably, the catalyst/feedstock weight ratio is from 2 to 200.

The process according to the present invention may be carried out in a fixed bed. However, this would imply that extremely high space velocities be required to attain the short contact times envisaged. Therefore, the present process is preferably carried out in a moving bed. The bed of catalyst may move upwards or downwards. When the bed moves upwards a process similar to a fluidized catalytic cracking process is obtained. Preferably, the process is carried out in a downwardly moving bed.

During the process some coke forms on the catalyst. Therefore, it is advantageous to regenerate the catalyst. Preferably the catalyst is regenerated by subjecting it, after having been contacted with the feedstock, to a treatment with an oxidizing gas, such as air. A continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

The coke formation does not occur at a very high rate. Hence, it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone, e.g. a moving bed, is longer than the residence time of the feedstock in the reaction zone. Of course the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

The feedstock which is to be converted in the present process comprises hydrotreated and/or hydrocracked hydrocarbons, preferably, though not necessarily, heavy feedstocks. Suitable feedstocks are obtained by hydrotreating and/or hydrocracking heavy flashed distillate fractions from long residue or deasphalted oils obtained from short residue. The feedstock is suitably fractionated to remove lower boiling fractions after hydrotreating and/or hydrocracking and prior to contacting with the zeolitic catalyst in accordance with the invention.

The product obtained by the process of the invention is optionally fractionated to yield an olefin-rich gas fraction, a gasoline fraction and a bottom fraction, all or part of which is optionally recycled to the feedstock upstream of the hydrotreating and/or hydrocracking unit. In this way, high conversion of the heavy deasphalted oil or heavy flashed distillate feedstock to more valuable olefin-rich gas is obtained. Therefore, in accordance with a further aspect of the invention, there is provided a process for the conversion of a hydrocarbonaceous feedstock comprising hydrotreating and/or hydrocracking said feedstock in the presence of a suitable catalyst, contacting at least a part of the hydrotreated and/or hydrocracked product with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.4 to 0.7 nm at a temperature of greater than 480 °C and a pressure of up to 10 bar during less than 10 seconds, fractionating the resulting converted material and recycling a heavier fraction to said hydrotreating and/or hydrocracking step.

The said hydrotreating step is known in the art and may be carried out at known conditions. Suitable conditions include a temperature of 150 to 400 °C, a hydrogen (partial) pressure of 30 to 150 bar, a space velocity of 0.5 to 4.0 kg/l.h and a hydrogen/feedstock ratio of 100 to 2000 NV/kg. Suitable hydrotreating catalysts comprise nickel, cobalt, tungsten, molybdenum, platinum, palladium or mixtures thereof on a carrier, such as alumina, silica-alumina, silica, zirconia, zeolites and the like. The catalyst may further comprise fluorine, phosphorus and/or boron. The temperature, gas rate and space velocity can be selected by the person skilled in the art, suitably from the range given above.

Hydrocracking is also known in the art and may be carried out under known conditions, such as over a hydrocracking catalyst at a temperature of 300 to 450 °C, a hydrogen (partial) pressure of 50 to 200 bar, a space velocity of 0.5 to 2.0 kg/l.catalyst.h and a H₂/mineral oil fraction ratio of 500 to 2000 NV/kg. The hydrocracking catalyst can be selected from any hydrocracking catalyst known in the art. Suitably the hydrocracking catalyst comprises a carrier and at least one hydrogenating metal or a compound thereof, which carrier has been selected from the group consisting of silica, alumina, silica-alumina and the faujasite-type zeolites. The most preferred faujasite-type zeolite is zeolite Y. The most preferred

hydrogenating metals are nickel, cobalt, tungsten and molybdenum and mixtures thereof, but platinum and/or palladium may also be used. The catalyst may further comprise fluorine and/or phosphorus and/or boron. When nickel, cobalt, molybdenum and/or tungsten are used as hydrogenating metal, they are preferably present in the form of their sulphides.

One of the advantages of the present invention over the process according to US 4,171,257 resides in the fact that a feedstock with a nitrogen content greater than 5 ppmw may be used with substantially no effect on the catalyst activity. Suitable feedstocks may have a nitrogen content of more than 10 ppmw calculated as nitrogen. The feedstock may even have a nitrogen content of 1000 ppmw or more, calculated as nitrogen.

The invention will now be further described with reference to the following examples and the accompanying drawing:

EXAMPLE 1

The feedstock in this example was a hydrotreated Arabian light deasphalted oil having the following properties:

IBP, °C	453
50 %wt	591
67 %wt	620
density 70/4	0.8532 kg/l
sulphur	232 ppmw
nitrogen	12 ppmw

The DAO feedstock was upgraded in a downflow reactor by passing it downwards co-currently with a flow of catalyst particles. The catalyst comprised ZSM-5 in an alumina matrix (weight ratio ZSM-5/alumina 1:3). The experiment was carried out at atmospheric pressure. Further process conditions and the results of the experiment are given in Table 1 below.

TABLE 1

Process conditions:	
Reactor temperature, °C	531
Catalyst/oil ratio, g/g	4.3
Contact time, s	2.2
Product, %w on feed	
C ₁	1.0
C ₂	1.2
C ₂	4.9
C ₃	2.0
C ₃	17.9
C ₄	2.1
C ₄	16.4
C ₅ -221 °C	26.3
221-450 °C	18.2
450 °C+	9.1
Coke	0.8
Conversion of 450 °C+ feed, %w	91

~ 997 °F

From the above results it will be seen that a high proportion of the gaseous products was olefinically unsaturated and the product contained a comparatively high proportion of middle distillates.

EXAMPLE 2

The feedstock in this example was a hydrocracked heavy flashed distillate having the following properties:

IBP, °C	330
---------	-----

Continuation of the Table on the next page

50 %wt	432
FBP, °C	620
fraction boiling below 370 °C, %wt	7.7
density 70/4	0.8157 kg/l
sulphur	20 ppmw
nitrogen	2 ppmw

The experiment was carried out as described in Example 1, but using the process conditions described in Table 2 below to give the results given in Table 2.

TABLE 2

Process conditions:	
Reactor temperature, °C	579
Catalyst/oil ratio, g/g	141
Contact time, s	1.7
Product, %w on feed	
C ₁	1.6
C ₂	1.0
C ₂	14.7
C ₃	3.9
C ₃	37.3
C ₄	4.6
C ₄	18.8
C ₅ -221 °C	8.6
221-370 °C	2.3
370 °C+	0.4
Coke	6.3
Conversion of 370 °C+, %w	99.6

EXAMPLE 3

This example employed as feedstock an Arabian heavy flashed discillate which, after initial hydrocracking, typically had the properties given in Table 3 below.

The flashed distillate was treated in accordance with the process illustrated in Fig. 1 as follows.

Feedstock was introduced on line 1, after mixing with hydrogen from line 2, to a hydrotreating/hydrocracking unit 3 operated at 90 bar hydrogen partial pressure at 400 °C with a suitable Ni/Mo/alumina hydrotreating catalyst.

The hydrotreated product was fractionated in unit 4 into a gaseous fraction 5, a naphtha fraction 6, a kerosine fraction 7, a gas oil fraction 8 and a bottoms fraction 9. Under conditions as described herein, bottoms fraction 9 was passed to a downflow reactor 10 as described in Example 1, containing catalyst as described in Example 1 and provided with suitable regeneration means from which coke can be removed in line 11 when necessary, while gaseous and liquid product is separated in fractionation unit 12 into a gaseous product 13, a gasoline product 14 and a bottoms stream 15, which is recycled to the feedstock in line 1 for re-processing.

Bottoms fraction 9 which is upgraded in reactor 10 comprises about 69% by weight based on the initial feed in line 1 when fractionated in unit 12. The composition of the fraction obtained from unit 12 is given in Table 3 below:

TABLE 3

Hydrocracked feedstock	
Refractive index, n_D^{20}	1.4720

Continuation of the Table on the next page

TABLE 3 (continued)

Hydrocracked feedstock	
UV aromatics, mmol/100 g	
mono	25
di	4
poly	3
Initial boiling point, °C	340
50 %wt	420
Final boiling point	540
Product, %w on feed	
Gas (C ₁₋₄)	31.5
H ₂	0.1
C ₁	0.7
C ₂₌	0.8
C ₂	3.4
C ₃₌	1.4
C ₃	12.3
C ₄₌	1.5
C ₄	11.3
Gasoline (C ₅ -221 °C)	18.5
Coke	0.5
Recycle (221+ °C)	19

It will be seen from the above results that the bottoms component separated from the initial flashed distillate has yielded a high proportion of olefinically unsaturated gaseous products and gasoline while the recycling facility enables maximum upgrading to more valuable products.

Claims

1. A process for the conversion of a hydrotreated and/or hydrocracked hydrocarbonaceous feedstock to obtain a high proportion of olefinically unsaturated gaseous products, which process comprises contacting the feedstock in a single stage, with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.4 to 0.7 nm characterized in that the contacting is carried out at a catalyst/feedstock weight ratio from 2 to 200, a temperature of greater than or equal to 480 °C and a pressure of up to 10 bar during less than 10 seconds.
2. A process according to claim 1 wherein the feedstock is contacted with the zeolitic catalyst during 1 to 6 seconds.
3. A process according to claim 1 or 2 wherein the temperature is 480 to 900 °C.
4. A process according to any one of the preceding claims wherein the zeolite is selected from crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.
5. A process according to any one of the preceding claims in which the zeolite is substantially in its hydrogen form.
6. A process according to any one of the preceding claims which is carried out in the absence of added hydrogen or steam.
7. A process according to any one of the preceding claims which is carried out in an upward or downward moving bed.
8. A process according to any one of the preceding claims wherein the feedstock is a hydrotreated and/or hydrocracked deasphalted oil or heavy flashed distillate.
9. A process according to any one of the preceding claims comprising pretreating the feedstock in a hydrotreating

and/or hydrocracking step in the presence of a suitable catalyst, fractionating the converted material obtained by the process of any one of the preceding claims and recycling a heavier fraction to said hydrotreating and/or hydrocracking step.

5

Patentansprüche

1. Verfahren für die Umwandlung eines wasserstoffbehandelten und/oder wasserstoffgecrackten kohlenwasserstoff-
haltigen Ausgangsmaterials, um einen hohen Anteil an olefinisch ungesättigten gasförmigen Produkten zu erhalten,
bei dem man das Ausgangsmaterial in einem einzigen Schritt mit einem zeolithischen Katalysator aus einem Zeo-
lithen mit einem Porendurchmesser von 0,4 bis 0,7 nm kontaktiert, dadurch gekennzeichnet, daß man die Kontakt-
behandlung bei einem Katalysator/Ausgangsmaterial-Gewichtsverhältnis von 2 bis 200, einer Temperatur von
480°C oder höher und einem Druck von bis zu 10 bar innerhalb von weniger als 10 Sekunden durchführt.
2. Verfahren nach Anspruch 1, in dem man das Ausgangsmaterial mit dem zeolithischen Katalysator innerhalb von
ein bis 6 Sekunden kontaktiert.
3. Verfahren nach Anspruch 1 oder 2, in dem die Temperatur zwischen 480 und 900°C liegt.
4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem man den Zeolithen aus kristallinen Metallsilikaten
mit ZSM-5-Struktur, Ferrierit, Erionit und deren Gemischen auswählt.
5. Verfahren nach einem der vorhergehenden Ansprüche, in dem der Zeolith überwiegend in seiner Wasserstoffform
vorliegt.
6. Verfahren nach einem der vorhergehenden Ansprüche, das man ohne Wasserstoff- oder Dampfzusatz durchführt.
7. Verfahren nach einem der vorhergehenden Ansprüche, das man in einem von unten nach oben oder von oben
nach unten wandernden Wanderbett durchführt.
8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Ausgangsmaterial ein wasserstoffbehandeltes
und/oder wasserstoffgecracktes entasphaltiertes Öl oder schweres Vakuumdestillat ist.
9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem man das Ausgangsmaterial zunächst einer Was-
serstoffbehandlung und/oder einem Wasserstoffcracken in Gegenwart eines geeigneten Katalysators unterzieht,
das nach dem Verfahren eines der vorhergehenden Ansprüche umgewandelte Material fraktioniert und die schwe-
rere Fraktion wieder besagter Wasserstoffbehandlung und/oder besagtem Wasserstoffcracken zuführt.

Revendications

1. Procédé de conversion d'une charge de départ hydrocarbonée, hydrotraitée et/ou hydrocraquée, en vue d'obtenir
une proportion élevée de produits gazeux à insaturation éthylénique, procédé qui comprend la mise en contact de
la charge de base, au cours d'une étape unique, avec un catalyseur zéolithique comprenant une zéolite possédant
un diamètre des pores de 0,4 à 0,7 nm, caractérisé en ce que l'on entreprend la mise en contact avec un rapport
pondéral catalyseur/charge de départ de 2 à 200, à une température égale ou supérieure à 480°C et une pression
allant jusqu'à 10 bars pendant une période inférieure à 10 secondes.
2. Procédé suivant la revendication 1, caractérisé en ce que l'on met la charge de départ en contact avec le catalyseur
zéolithique pendant 1 à 6 secondes.
3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que la température varie de 480 à 900°C.
4. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que l'on choisit la zéolite parmi
les silicates de métaux cristallins possédant une structure ZSM-5, la ferrièreite, l'érionite et leurs mélanges.
5. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la zéolite se présente
sensiblement sous sa forme hydrogène.

6. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'on l'entreprend en l'absence de vapeur d'eau ou d'hydrogène ajouté.
7. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'on l'entreprend dans un lit mobile ascendant ou descendant.
8. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la charge de base est un distillat de flashing lourd ou une huile désasphaltée hydrotraitee et/ou hydrocraquée.
9. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce qu'il comprend le traitement préalable de la charge de base au cours d'une étape d'hydrotraitement et/ou d'hydrocraquage en présence d'un catalyseur approprié, le fractionnement de la matière convertie obtenue par mise en oeuvre du procédé suivant l'une quelconque des revendications précédentes et le recyclage d'une fraction lourde vers l'étape d'hydrotraitement et/ou d'hydrocraquage précitée.

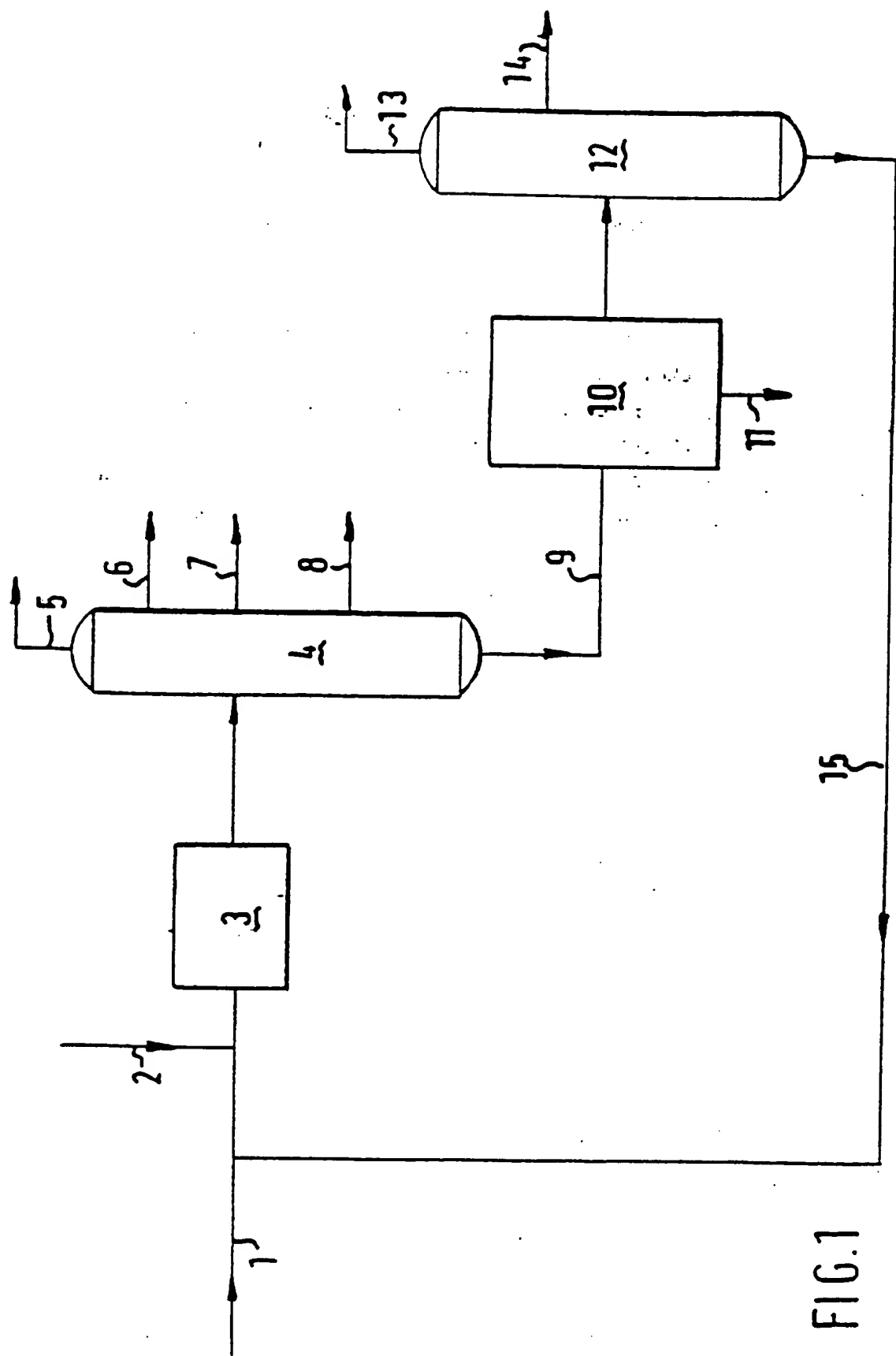


FIG. 1